

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-145104

(43)Date of publication of application : 06.06.1995

(51)Int.Cl.

C07C 69/33  
B01F 17/42  
C07C 67/08  
C08G 65/32  
// C11D 1/68

(21)Application number : 05-293552

(71)Applicant : MITSUBISHI CHEM CORP

(22)Date of filing : 24.11.1993

(72)Inventor : KASORI YUKIO  
YAMAZAKI YASUSHI  
UMEZAWA TOMOAKI

## (54) PRODUCTION OF POLYGLYCEROL FATTY ACID ESTERS

## (57)Abstract:

PURPOSE: To obtain polyglycerol fatty acid esters of high monoester content by esterification of fatty acid with polyglycerol to a certain esterification degree followed by continuation of the reaction at a increased temperature.

CONSTITUTION: Polyglycerol is allowed to react with a fatty acid to give a polyglycerol fatty acid ester (PoGE). At this time, the reaction temperature is set to from 180 to 260° C at least until the conversion of the fatty acid reaches at least 70%. Then, the reaction temperature is raised further by 10 to 50° C and the reaction is continued. The polyglycerol used or a raw material has 4 to 14 average polymerization degree and 1100 to 850 hydroxyl value. The fatty acid is, for example, stearic, oleic, palmitic or lauric acid, etc. According to the process, rearrangement occurs between highly substituted PoGE of di- or higher esters and unreactig polyglycerol to give monoesters. PoGE is approved as a food additive, a safe surfactant, and is used as a food emulsifier or a food solubilizer.

## LEGAL STATUS

[Date of request for examination]

07.06.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3301182

[Date of registration]

26.04.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

**\* NOTICES \***

**Japan Patent Office is not responsible for any damages caused by the use of this translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**CLAIMS**

---

[Claim(s)]

[Claim 1] The manufacture approach of the polyglyceryl fatty acid ester which makes reaction temperature until the conversion ratio of a fatty acid reaches to at least 70% 180 degrees C - 260 degrees C in the approach of making polyglycerin and a fatty acid reacting and manufacturing polyglyceryl fatty acid ester, and is characterized by raising further 10-50 degrees C of reaction temperature, and making it react after that.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of detailed PoGE with many monoester components about polyglyceryl fatty acid ester (it abbreviates to PoGE hereafter).

[0002]

[Description of the Prior Art] Conventionally, although PoGE is known as a surfactant with the high safety approved as a food additive and it is used mainly as a food-grade emulsifier or a solubilizing agent, the use to cosmetics, food and a food-grade cleaning agent (JP,59-187096,A, a 60-53599 official report, a 60-149699 official report, 62-27493 official report), an oral cavity internal use constituent (JP,62-45513,A, 63-60917 official report), etc. is tried further.

[0003] As a process of PoGE, the approach by the esterification reaction of polyglycerin and a fatty acid is usually learned (JP,62-45513,A). This reaction has good reactivity, and it is made to react, distilling off generation water out of the system of reaction using a small amount of alkali catalyst. Moreover, although reaction temperature changes with classes of fatty acid, it is usually about 180-260 degrees C. If it reacts at an elevated temperature not much, a fault reaction and volatilization of a fatty acid happen and are disadvantageous. One of the troubles of this approach is that PoGE with many monoester object contents with the largest application is difficult to get. That is, in PoGE which unreacted polyglycerin remained so much and generated in one side in the product by this approach even if it presented the reaction with a fatty acid and polyglycerin by the mole ratio of 1:1, PoGE of whenever [ more than diester / high permutation ] is \*\*\*\*\* rare \*\*\*\*\*.

[0004]

[Problem(s) to be Solved by the Invention] In case this invention makes polyglycerin and a fatty acid react in view of the above-mentioned actual condition, it tends to offer the manufacture approach of PoGE with many monoester object contents.

[0005]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of repeating examination wholeheartedly, after this invention person etc. advanced the esterification reaction of polyglycerin and a fatty acid to some extent, by pulling up the temperature of a reaction mixture and continuing a reaction, he found out that PoGE with many monoester object contents was obtained, and completed this invention.

[0006] That is, this invention consists in the manufacture approach of PoGE which makes reaction temperature until the conversion ratio of a fatty acid reaches to at least 70% 180 degrees C - 260 degrees C, and is characterized by raising further 10-50 degrees C of reaction temperature, and making it react after that in the approach of making polyglycerin and a fatty acid reacting and manufacturing PoGE. Hereafter, this invention is explained to a detail. In this invention, average degree of polymerization usually uses the thing of 4-14, and hydroxyl values 1100-850 as raw material polyglycerin. Stearin acid, oleic acid, a palmitic acid, and a lauric acid are usually mentioned, using the fatty acid of the saturation of C8-C22, or partial saturation as a raw material fatty acid. the amount of polyglycerin and the fatty acid used -- it is going to manufacture -- although it changes with presentations of PoGE -- polyglycerin -- receiving -- 0.01-10-mol twice -- it is 0.1-5-mol twice preferably. If there is too much amount of the fatty acid used, what has many monoester object contents is not made, and if too few, the amount of generation of PoGE will decrease.

[0007] At the reaction of this invention, although a solvent may be used, the polyglycerin of an excessive amount is usually used to serve also as a solvent. In addition, although unreacted polyglycerin will remain in a reaction mixture in this case, this is removable by approaches, such as solvent extraction. Moreover, the mixture which contained polyglycerin depending on the field of the invention may be used as it is.

[0008] Although the reaction of this invention may be performed with a non-catalyst, an alkali catalyst is usually used. as an alkali catalyst -- K<sub>2</sub> CO<sub>3</sub>, KOH, Na<sub>2</sub> CO<sub>3</sub>, NaOH, etc. -- it is -- polyglycerin -- receiving -- 5x10<sup>-7</sup>-1-mol twice -- desirable -- a 5x10<sup>-6</sup>-0.1-mol time -- it uses. Reaction temperature until the conversion ratio of a fatty acid reaches to at least 70% is 180-260 degrees C, and is 200-250 degrees C preferably. Reaction time is usually 0.5 - 15 hours.

[0009] A reaction is usually heated to predetermined temperature, teaching and agitating polyglycerin, a fatty acid, and a catalyst to a mixing vessel type reactor, and it is performed, distilling off generation water out of the system of reaction. In this invention, in an esterification reaction, 70% or more, preferably, the conversion ratio of a fatty acid reacts with said reaction temperature until it reaches to 95% or more still more preferably, and it continues a reaction rather than this temperature after that 80% or more at 10-50 degrees

C and desirable temperature high 10–30 degrees C. Although the reaction time after this temperature up changes with conversion ratios of the fatty acid at the time of carrying out a temperature up, it is 1 – 4 hours preferably from the time of the conversion ratio of a fatty acid becoming 100% for 0.5 to 6 hours. Reaction time is suitably chosen according to the fatty acid of a raw material, and the mole ratio of polyglycerin within the limits of this, for example, is [ at a fatty acid / polyglycerin =1.0 mole ratio ] 4 hours in a fatty acid / polyglycerin =0.3 mole ratio in a fatty acid / polyglycerin =5.0 mole ratio for 2 hours for 1 hour. If this reaction time is too short, it is difficult to make [ many ] the content of the monoester object in Generation PoGE. Moreover, as for the reactor gaseous-phase section, it is desirable during a series of reactions to circulate inert gas, such as nitrogen gas. Removal of the polyglycerin which remains after reaction termination and in a reaction mixture should just add the usual purification means for solvent extraction etc.

[0010]

[Effect of the Invention] The rearrangement of a fatty-acid radical produces this invention between PoGE of a high substitution product more than the once generated diester, and unreacted polyglycerin, and it is thought that a monoester object generates. Therefore, compared with the conventional manufacture approach, PoGE with many contents of a monoester object is obtained.

[0011]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited to description of an example, unless the summary is exceeded.

Example 1 polyglycerin (average-degree-of-polymerization 10.9, average-molecular-weight 825, hydroxyl value 888 mgKOH/g) 11.0kg and 3.69kg (mixture of the weight ratio 3:1 of stearin acid and a palmitic acid) (the mole ratio of a raw material fatty acid and polyglycerin is 1:1) of fatty acids After having added 3.5ml of 10wt% caustic-alkali-of-sodium water solutions after teaching the churning mold reactor equipped with the heating jacket and carrying out a temperature up to 240 degrees C, and performing an esterification reaction for 2.25 hours (the conversion ratio of the fatty acid at this time was 99%), the temperature up of this reaction mixture was carried out to 260 degrees C, and the reaction was performed for 4 hours. The content of a monoester object was analyzed on the below-mentioned LC analysis conditions after reaction termination. The result was described in Table -1.

[0012] After performing an esterification reaction at 2–3240 degrees C of examples for 2.25 hours, it carried out by the same approach as an example 1 except having carried out the temperature up to the temperature shown in Table -1, and having performed the reaction for 4 hours. The result was described in Table -1. It carried out by the same approach as an example 1 except having ended the reaction, without performing the reaction after the temperature up of example of comparison 1 reaction mixture. The result was described in Table -1.

[0013] It carried out by the approach of the example 1 of a comparison, and the same approach except having made reaction time after example of comparison 2 temperature up into 4 hours. The result was described in Table -1.

[0014]

[Table 1]

表-1

|       | 昇温後の反応応    |             | P o G E 組成           |                     | 未反応<br>ポリグリ<br>セリン<br>(w t %) |
|-------|------------|-------------|----------------------|---------------------|-------------------------------|
|       | 温 度<br>(℃) | 時 間<br>(hr) | モノエステル体<br>(L C 面積%) | 多エステル体<br>(L C 面積%) |                               |
| 実施例 1 | 2 6 0      | 4           | 7 4                  | 2 6                 | 4 3                           |
| " 2   | 2 7 0      | 4           | 7 7                  | 2 3                 | 4 0                           |
| " 3   | 2 8 0      | 4           | 7 8                  | 2 2                 | 4 0                           |
| 比較例 1 | —          | —           | 4 7                  | 5 3                 | 7 0                           |
| " 2   | 2 4 0      | 4           | 5 0                  | 5 0                 | 6 8                           |

[0015]

[Table 2]

<LC analysis conditions> Equipment Shimadzu LC-10A column Asahi pak ODS 6x150mm carrier H2 O/(MeOH:THF=1:2) Detector with 0.7 ml/min GURAJIENTO ELSD (EBAPORETIBU light sputtering detector) 125 degrees C N2 55mm (gage)

Sample It is after acetylation processing by the pyridine + acetic anhydride. 20microl Pour in.

[Translation done.]

**\* NOTICES \***

**Japan Patent Office is not responsible for any damages caused by the use of this translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**TECHNICAL FIELD**

---

[Industrial Application] This invention relates to the manufacture approach of detailed PoGE with many monoester components about polyglyceryl fatty acid ester (it abbreviates to PoGE hereafter).

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**PRIOR ART**

---

[Description of the Prior Art] Conventionally, although PoGE is known as a surfactant with the high safety approved as a food additive and it is used mainly as a food-grade emulsifier or a solubilizing agent, the use to cosmetics, food and a food-grade cleaning agent (JP,59-187096,A, a 60-53599 official report, a 60-149699 official report, 62-27493 official report), an oral cavity internal use constituent (JP,62-45513,A, 63-60917 official report), etc. is tried further.

[0003] As a process of PoGE, the approach by the esterification reaction of polyglycerin and a fatty acid is usually learned (JP,62-45513,A). This reaction has good reactivity, and it is made to react, distilling off generation water out of the system of reaction using a small amount of alkali catalyst. Moreover, although reaction temperature changes with classes of fatty acid, it is usually about 180-260 degrees C. If it reacts at an elevated temperature not much, a fault reaction and volatilization of a fatty acid happen and are disadvantageous. One of the troubles of this approach is that PoGE with many monoester object contents with the largest application is difficult to get. That is, in PoGE which unreacted polyglycerin remained so much and generated in one side in the product by this approach even if it presented the reaction with a fatty acid and polyglycerin by the mole ratio of 1:1, PoGE of whenever [ more than diester / high permutation ] is \*\*\*\*\* rare \*\*\*\*\*.

---

[Translation done.]

**\* NOTICES \***

**Japan Patent Office is not responsible for any damages caused by the use of this translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**EFFECT OF THE INVENTION**

---

[Effect of the Invention] The rearrangement of a fatty-acid radical produces this invention between PoGE of a high substitution product more than the once generated diester, and unreacted polyglycerin, and it is thought that a monoester object generates. Therefore, compared with the conventional manufacture approach, PoGE with many contents of a monoester object is obtained.

---

[Translation done.]

**\* NOTICES \***

**Japan Patent Office is not responsible for any damages caused by the use of this translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

[Problem(s) to be Solved by the Invention] In case this invention makes polyglycerin and a fatty acid react in view of the above-mentioned actual condition, it tends to offer the manufacture approach of PoGE with many monoester object contents.

---

[Translation done.]



**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**MEANS**

---

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of repeating examination wholeheartedly, after this invention person etc. advanced the esterification reaction of polyglycerin and a fatty acid to some extent, by pulling up the temperature of a reaction mixture and continuing a reaction, he found out that PoGE with many monoester object contents was obtained, and completed this invention.

[0006] That is, this invention consists in the manufacture approach of PoGE which makes reaction temperature until the conversion ratio of a fatty acid reaches to at least 70% 180 degrees C - 260 degrees C, and is characterized by raising further 10-50 degrees C of reaction temperature, and making it react after that in the approach of making polyglycerin and a fatty acid reacting and manufacturing PoGE. Hereafter, this invention is explained to a detail. In this invention, average degree of polymerization usually uses the thing of 4-14, and hydroxyl values 1100-850 as raw material polyglycerin. Stearin acid, oleic acid, a palmitic acid, and a lauric acid are usually mentioned, using the fatty acid of the saturation of C8-C22, or partial saturation as a raw material fatty acid. the amount of polyglycerin and the fatty acid used — it is going to manufacture — although it changes with presentations of PoGE — polyglycerin — receiving — 0.01-10-mol twice — it is 0.1-5-mol twice preferably. If there is too much amount of the fatty acid used, what has many monoester object contents is not made, and if too few, the amount of generation of PoGE will decrease.

[0007] At the reaction of this invention, although a solvent may be used, the polyglycerin of an excessive amount is usually used to serve also as a solvent. In addition, although unreacted polyglycerin will remain in a reaction mixture in this case, this is removable by approaches, such as solvent extraction. Moreover, the mixture which contained polyglycerin depending on the field of the invention may be used as it is.

[0008] Although the reaction of this invention may be performed with a non-catalyst, an alkali catalyst is usually used. as an alkali catalyst —  $K_2CO_3$ , KOH,  $Na_2CO_3$ , NaOH, etc. — it is — polyglycerin — receiving —  $5 \times 10^{-7}$ -1-mol twice — desirable — a  $5 \times 10^{-6}$ -0.1-mol time — it uses. Reaction temperature until the conversion ratio of a fatty acid reaches to at least 70% is 180-260 degrees C, and is 200-250 degrees C preferably. Reaction time is usually 0.5 - 15 hours.

[0009] A reaction is usually heated to predetermined temperature, teaching and agitating polyglycerin, a fatty acid, and a catalyst to a mixing vessel type reactor, and it is performed, distilling off generation water out of the system of reaction. In this invention, in an esterification reaction, 70% or more, preferably, the conversion ratio of a fatty acid reacts with said reaction temperature until it reaches to 95% or more still more preferably, and it continues a reaction rather than this temperature after that 80% or more at 10-50 degrees C and desirable temperature high 10-30 degrees C. Although the reaction time after this temperature up changes with conversion ratios of the fatty acid at the time of carrying out a temperature up, it is 1 - 4 hours preferably from the time of the conversion ratio of a fatty acid becoming 100% for 0.5 to 6 hours. Reaction time is suitably chosen according to the fatty acid of a raw material, and the mole ratio of polyglycerin within the limits of this, for example, is [ at a fatty acid / polyglycerin = 1.0 mole ratio ] 4 hours in a fatty acid / polyglycerin = 0.3 mole ratio in a fatty acid / polyglycerin = 5.0 mole ratio for 2 hours for 1 hour. If this reaction time is too short, it is difficult to make [ many ] the content of the monoester object in Generation PoGE. Moreover, as for the reactor gaseous-phase section, it is desirable during a series of reactions to circulate inert gas, such as nitrogen gas. Removal of the polyglycerin which remains after reaction termination and in a reaction mixture should just add the usual purification means for solvent extraction etc.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## EXAMPLE

[Example] Next, although an example explains this invention to a detail further, this invention is not limited to description of an example, unless the summary is exceeded.

Example 1 polyglycerin (average-degree-of-polymerization 10.9, average-molecular-weight 825, hydroxyl value 888 mgKOH/g) 11.0kg and 3.69kg (mixture of the weight ratio 3:1 of stearin acid and a palmitic acid) (the mole ratio of a raw material fatty acid and polyglycerin is 1:1) of fatty acids After having added 3.5ml of 10wt% caustic-alkali-of-sodium water solutions after teaching the churning mold reactor equipped with the heating jacket and carrying out a temperature up to 240 degrees C, and performing an esterification reaction for 2.25 hours (the conversion ratio of the fatty acid at this time was 99%), the temperature up of this reaction mixture was carried out to 260 degrees C, and the reaction was performed for 4 hours. The content of a monoester object was analyzed on the below-mentioned LC analysis conditions after reaction termination. The result was described in Table -1.

[0012] After performing an esterification reaction at 2-3240 degrees C of examples for 2.25 hours, it carried out by the same approach as an example 1 except having carried out the temperature up to the temperature shown in Table -1, and having performed the reaction for 4 hours. The result was described in Table -1. It carried out by the same approach as an example 1 except having ended the reaction, without performing the reaction after the temperature up of example of comparison 1 reaction mixture. The result was described in Table -1.

[0013] It carried out by the approach of the example 1 of a comparison, and the same approach except having made reaction time after example of comparison 2 temperature up into 4 hours. The result was described in Table -1.

[0014]

[Table 1]

表-1

|       | 昇温後の反応応    |             | P o G E 組成         |                   | 未反応<br>ポリグリ<br>セリン<br>(w t %) |
|-------|------------|-------------|--------------------|-------------------|-------------------------------|
|       | 温 度<br>(℃) | 時 間<br>(hr) | モノエステル体<br>(LC面積%) | 多エステル体<br>(LC面積%) |                               |
| 実施例 1 | 2 6 0      | 4           | 7 4                | 2 6               | 4 3                           |
| " 2   | 2 7 0      | 4           | 7 7                | 2 3               | 4 0                           |
| " 3   | 2 8 0      | 4           | 7 8                | 2 2               | 4 0                           |
| 比較例 1 | —          | —           | 4 7                | 5 3               | 7 0                           |
| " 2   | 2 4 0      | 4           | 5 0                | 5 0               | 6 8                           |

[0015]

[Table 2]

<LC analysis conditions> Equipment Shimadzu LC-10A column Asahi pak ODS 6x150mm carrier H2 O/(MeOH:THF=1:2) Detector with 0.7 ml/min GURAJIENTO ELSD (EBAPORETIBU light sputtering detector) 125 degrees C N2 55mm (gage)

Sample It is after acetylation processing by the pyridine + acetic anhydride. 20microl Pour in.

[Translation done.]